

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 882 786 A1**

(12)

**EUROPEAN PATENT APPLICATION**

published in accordance with Art. 158(3) EPC

(43) Date of publication:

09.12.1998 Bulletin 1998/50

(51) Int. Cl.<sup>6</sup>: **C11D 1/83**, C11D 3/33,

C11D 3/08, C11D 3/37,

C11D 17/06

(21) Application number: **97900464.5**

(22) Date of filing: **21.01.1997**

(86) International application number:

**PCT/JP97/00110**

(87) International publication number:

**WO 97/27278 (31.07.1997 Gazette 1997/33)**

(84) Designated Contracting States:

**DE FR GB**

(30) Priority: **22.01.1996 JP 8559/96**

**21.02.1996 JP 33787/96**

**19.04.1996 JP 98176/96**

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(54) **HIGH-DENSITY POWDERED DETERGENT COMPOSITION**

(57) A high-density powdered detergent composition which has a bulk density of 0.6 to 1.2 g/ml and which comprises 0.5 to 30% by weight of (a) a glycine-N,N-diacetic acid derivative, 5 to 45% by weight of (b) a nonionic surfactant having an HLB value of 10.5 to 15.0, 0.5 to 18% by weight of (c) an anionic surfactant and 1 to 30% by weight of (d) an aluminosilicate, each percentage being based on the total weight of the composition, and the weight ratio of the component (b) to the component (c) lying between 90 : 1 and 60 : 40. This composition contains both a glycine-N,N-diacetic acid derivative which is a builder excellent in biodegradability and sequestering power and an inorganic builder such as zeolite or crystalline silicate, and exhibits high detergency.

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## Description

### Background of the Invention

#### 5 Field of the Invention:

The present invention relates to a high-density powdered detergent composition. In particular, it relates to a high-density powdered detergent composition exhibiting high detergency and containing an organic builder excellent in biodegradability.

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#### Description of Related Art:

A detergent composition for clothes is basically composed of a surfactant which solubilizes soil, separates it from fibers, and dissolves or disperses it in a washing solution, an alkaline substance which accelerates the decomposition or solubilization of soil, a high-molecular compound which suspends soil in a washing solution, a sequestering agent which removes substances lowering the power of surfactants, for example, calcium or magnesium ions from a washing solution, and so on.

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Among these components, "builders for detergents" generally refer to substances which do not exhibit detergency per se but can enhance the detergency of a surfactant when used together with the surfactant. Among such builders for detergents, the above-mentioned sequestering agent serves to make a surfactant exhibit its performance more effectively, thus being one of the extremely important builders for detergents.

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Phosphate salts such as sodium tripolyphosphate were formerly added to detergents for clothes as the sequestering agent. However, such phosphate salts are believed to be one of the factors causing the eutrophication of lakes, marshes and so on. In the detergent industry, therefore, the development of a detergent not containing any phosphate builder has been continued. As a result, a crystalline sodium aluminosilicate having a specific structure (which is called "zeolite" in the detergent industry) is currently used as the main component of the sequestering agent, because it is free from the above problem unlike phosphate builders and has recently been stabilized in the cost.

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Further, a detergent composition for clothes has changed in the form from the late 1980s, so that a so-called compact detergent which has a high bulk density and is lowered in the volume of the composition used per washing run is now widely used. However, the particles constituting such a compact detergent are more highly compacted than those constituting the detergent of the prior art, thus being problematic in solubility. In particular, zeolite which is one of the constituents of the compact detergent is insoluble in water per se, and therefore often causes the generation of water insolubles in conducting washing with the compact detergent. The applicant of the present invention have made attempts to solve this problem by exerting ingenuities in the formulation or production process of the compact detergent.

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However, such a solution is often accompanied with the restriction of the formulation. Under these circumstances, the development of a more excellent builder for detergents is being made for the purpose of attaining the progress of the industry.

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In addition to zeolite, crystalline silicates are also used as builders for detergents. For example, JP-A 60-227895 discloses the use of crystalline silicates as water softeners; JP-A 6-10000, 2-176398 and 7-53992 disclose detergent compositions containing crystalline silicates; and JP-A 5-184946 and 6-116588 disclose specific crystalline silicates and detergent compositions containing them.

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As described above, zeolite is a water-insoluble builder for detergents. On the other hand, water-soluble builders for detergents include organic builders such as salts of polycarboxylic acids, and specific examples of such salts include citrates, malates, salts of nitrilotriacetic acid (NTA), salts of ethylenediaminetetraacetic acid (EDTA) and polymers of carboxylated vinyl compounds. The term "polymers of carboxylated vinyl compounds" refers to, e.g., polyacrylate salts, salts of acrylic acid /maleic acid copolymers, and salts of olefin/maleic acid copolymers, whose molecular weights lie within the oligomeric region. However, concern is shown for the use of these organic builders, because the organic builders are disadvantageous in that the sequestering power is unsatisfactory, that the toxicity to fish has been pointed out and/or that the biodegradability is poor.

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From the standpoint of the influence on the environment, studies have recently been made on builders excellent in biodegradability and sequestering power. For example, specific organic builders prepared by the reaction of epoxysuccinic acid or maleic acid with aspartic acid and detergent compositions containing them are disclosed in JP-A 5-170714, and this patent document also describes that these builders are excellent in biodegradability and detergency-enhancing effect. Further, JP-A 6-248300 discloses a detergent composition containing an organic builder consisting of hydroxyiminodisuccinic acid salt in a specific amount. Furthermore, it has been reported by BASF that glycine-N,N-diacetic acid derivatives are excellent in biodegradability and sequestering power, and are therefore extremely suitable for builders for detergents (New Horizons' 95 Conference Lake George, New York, September 19-22, 1995). In the detergent composition reported in this conference, a surfactant mixture comprising 9% of FAS (a salt of sulfate ester of higher aliphatic

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alcohol) and 10% of a nonionic surfactant is used together with a glycine-N,N-diacetic acid derivative, zeolite, soda ash, perboric acid and/or TAED (tetraacetylenediamine).

Meanwhile, it is believed that there is a good possibility of further enhancing the detergency of a detergent composition containing a glycine-N,N-diacetic acid derivative as the organic builder. In particular, no optimum formulation has been found as yet with respect to a high-density detergent composition which comprises a surfactant component comprising a nonionic surfactant as the base and a proper amount of an anionic surfactant, and a builder component comprising both the above organic builder and an inorganic builder such as zeolite or crystalline silicate.

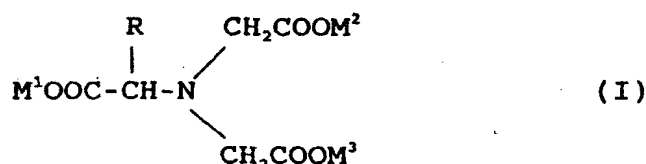
#### Disclosure of Invention

#### Summary of the Invention:

Under these circumstances, the present invention aims at providing a high-density detergent composition improved in detergency and comprising the above organic builder excellent in biodegradability, a surfactant component comprising a nonionic surfactant as the base and such an amount of an anionic surfactant as to permit the retention and development of the properties of the nonionic surfactant, and an inorganic builder.

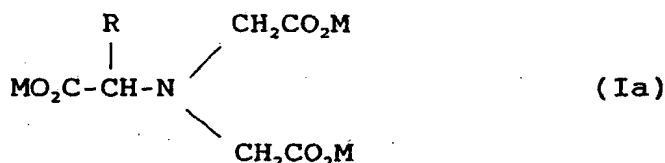
The inventors of the present invention have made extensive studies for attaining the above aim. As a result of the studies, they have found that the detergency of a surfactant system comprising a nonionic surfactant as the base and a nonionic surfactant at a specific weight ratio can be enhanced dramatically by adding both a glycine-N,N-diacetic acid derivative serving as an organic builder and an inorganic builder in specific proportions respectively to the system. The present invention has been accomplished on the basis of this finding.

Namely, the present invention provides a high-density powdered detergent composition which has a bulk density of 0.6 to 1.2 g/ml and which comprises 0.5 to 30% by weight of (a) a glycine-N,N-diacetic acid derivative represented by the following formula (I), 5 to 45% by weight of (b) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0, 0.5 to 18% by weight of (c) an anionic surfactant and 1 to 30% by weight of (d) an aluminosilicate, each percentage being based on the total amount of the composition and the weight ratio of the component (b) to the component (c) [i.e., the (b)/(c) weight ratio] lying between 90 : 1 and 60 : 40:



wherein R is C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>18</sub> alkenyl; and M<sup>1</sup>, M<sup>2</sup> and M<sup>3</sup> are each H, Na, K or NH<sub>4</sub>.

In other words, the present invention relates to a high-density powdered detergent composition which comprises 0.5 to 30% by weight of (a) a glycine-N,N-diacetic acid derivative represented by the following formula (Ia):



(wherein R is C<sub>1</sub>-C<sub>18</sub> alkyl or alkenyl; and M is H, Na, K or NH<sub>4</sub>), 5 to 45% by weight of (b) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0, 0.5 to 18% by weight of (c) an anionic surfactant and 1 to 30% by weight of (d) an aluminosilicate, the (b)/(c) weight ratio lying between 90 : 1 and 60 : 40, and which has a bulk density of 0.6 to 1.2 g/ml.

The high-density powdered detergent composition of the present invention will now be described in detail.

## Detailed Description of the Invention:

## ((a) Organic builder)

5 The organic builder to be used in the present invention is a glycine-N,N-diacetic acid derivative represented by the formula (I).

In the formula (I),  $M^1$ ,  $M^2$  and  $M^3$  (i.e., counter ions) are each generally hydrogen ion, sodium ion or potassium ion.

In the present invention, it is necessary from the standpoint of the detergency of the detergent composition that the organic builder (a) is contained in the composition in an amount of 0.5 to 30% by weight, preferably 2 to 15% by weight.

10 Specific examples of the compound (a) to be used in the present invention as the organic builder are disclosed in DE-A1 4319935, WO 94/29421 and so on. That is, the compounds (a) are known as builders to the public. However, what has been known about the compounds is only that the compounds function as ordinary builders for detergents. In the present invention, meanwhile, an organic builder is added to a system comprising a surfactant mixture exhibiting also ionic properties which comprises an anionic surfactant as the base and such an amount of an anionic surfactant as to permit the retention and development of the fundamental properties of the nonionic surfactant, and an inorganic builder. With respect to such a case, there is no information on which formulation can give the optimum detergency.

## ((b) Nonionic surfactant)

20 Examples of the nonionic surfactant to be used in the present invention include polyoxyalkylene alkyl ethers, polyoxyalkylene alkylphenyl ethers, fatty acid esters of polyoxyethylene sorbitan, fatty acid esters of polyoxyethylene sorbitol, fatty acid esters of polyethylene glycol, alkyl esters of polyoxyethylene fatty acids, polyoxyethylenepolyoxypropylene alkyl ethers, polyoxyethylenealkylamines, glycerol fatty acid esters, polyoxyethylene higher fatty acid esters, alkanolamides of higher fatty acids, alkanolamides of polyoxyethylene higher fatty acids, esters of fatty acids with polyhydric 25 alcohols, fatty acid esters of sucrose, alkylamine oxides, alkyl glycosides and alkylglucosamides. In the present invention, it is particularly suitable to use a polyoxyethylene alkyl ether prepared by the addition reaction of a linear or branched, primary or secondary alcohol having 10 to 18 carbon atoms, preferably 10 to 15, still preferably 12 to 14 carbon atoms with on the average 4 to 11, preferably 5 to 10 ethylene oxide molecules per molecule of the alcohol. However, the case wherein the above polyoxyethylene alkyl ether can favorably be used is limited to washing at about 25°C 30 which is popular in Japan or the like. For washing at about 60°C which is popular in Europe or the like, it is desirable to use a polyoxyethylene alkyl ether wherein the number of ethylene oxide molecules added is larger than that described above by about two.

Among the above nonionic surfactants, those being liquid or slurry at 40°C, i.e., those having a melting point of 40°C or below are excellent in the power of washing soil off, and foaming and defoaming properties, thus being favorable.

35 The nonionic surfactant to be used in the present invention must have an HLB value (as calculated by Griffin's method) of 10.5 to 15.0, preferably 11 to 14.

The component (b) is contained in the composition in an amount of 5 to 45% by weight, preferably 10 to 25% by weight. When the amount of the component (b) lies within this range, the detergent composition exhibits excellent detergency.

## ((c) Anionic surfactant)

45 Examples of the anionic surfactant include alkylbenzenesulfonic acid salts wherein the alkyl has 8 to 18 carbon atoms, salts of alkanesulfonic acids (SAS), salts of  $\alpha$ -olefinsulfonic acids, salts of sulfates of primary and secondary higher alcohols, salts of sulfates of polyoxyethylene alkyl ethers,  $\alpha$ -sulfofatty acid salts and higher fatty acid salts, among which higher fatty acid salts having 10 to 18 carbon atoms are preferable.

These anionic surfactants may be used each alone or as a mixture of two or more of them.

50 It is necessary from the standpoint of the detergency that the component (c) is contained in the composition in an amount of 0.5 to 18% by weight, preferably 2 to 10%.

Further, it is essential to the present invention that the weight ratio of the component (b) to the component (c) lies between 90 : 1 and 60 : 40, preferably 95 : 5 and 79 : 21.

## ((d) Aluminosilicate)

55 The aluminosilicate to be used in the present invention as the component (d) may be any of amorphous and crystalline ones.

It is preferable that the amorphous aluminosilicate be one containing silicon in an amount of 30% by weight or

above, still preferably 40% by weight or above in terms of  $\text{SiO}_2$ . Further, the use of such an amorphous aluminosilicate as to give a 5% dispersion (a dispersion of 5 g of a sample in 100 ml of water free from carbonic acid) having a pH of 9 or above brings about a detergent composition which exhibits excellent solubility even after the storage under high-humidity conditions. In other words, such an amorphous aluminosilicate is effective in protecting the detergent composition from the deterioration of solubility caused by storage under high-humidity conditions. The term "pH" used above with respect to a 5% amorphous aluminosilicate dispersion refers to a value as determined according to JIS K6220.

Examples of the amorphous aluminosilicate to be used in the present invention include those represented by the following formula (i):



wherein M is alkali metal; and a, b and c represents the molar proportions of the constituent components respectively. In general, a is a number of 0.7 to 2.0, b is a number of 0.8 or above but below 4, and c is an arbitrary positive number.

These amorphous aluminosilicates exhibit high oil absorption and high cation exchange capacity.

Among the above amorphous aluminosilicates, those represented by the following formula (ii) are particularly preferable:



wherein b is a number of 1.8 to 3.2; and c is a number of 1 to 6.

Such amorphous aluminosilicates can be prepared by referring to, e.g., the process disclosed in JP-A 6-179899 and EP-A 593014 corresponding thereto.

On the other hand, crystalline aluminosilicate is generally called "zeolite", and is represented by the following formula (iii):



wherein M is alkali metal; and a', b' and w represent the molar proportions of the constituent components respectively, with a', b' and w being generally a number of 0.7 to 1.5, a number of 0.8 or above but below 6, and an arbitrary positive number, respectively.

Among the above crystalline aluminosilicates, those represented by the following formula (iv) are particularly preferable:



wherein n is a number of 1.8 to 3.0; and w is a number of 1 to 6.

The crystalline aluminosilicate (zeolite) to be used in the present invention is desirably a synthetic zeolite having a mean primary particle diameter of 0.1 to 10  $\mu\text{m}$ , for example, zeolite A, X or P. The zeolite may be added in the form of a powder and/or a dry agglomerate prepared by drying a zeolite slurry.

In the present invention, it is necessary from the standpoint of the detergency of the resulting detergent composition that the aluminosilicate (d) is contained in the composition in an amount of 1 to 30% by weight, preferably 5 to 25% by weight.

Although the high-density powdered detergent composition of the present invention comprises the above components (a) to (d) as the essential components, it may further contain the following components.

#### (Crystalline silicate)

It is desirable from the standpoint of detergency that the high-density powdered detergent composition of the present invention contains a crystalline silicate. The crystalline silicate to be used in the present invention is preferably one essentially consisting of silicon dioxide ( $\text{SiO}_2$ ) and an alkali metal oxide (i.e., an alkali metal silicate), still preferably an alkali metal silicate having an  $\text{SiO}_2$  to  $\text{M}_2\text{O}$  ratio (wherein M is alkali metal) of 0.5 to 2.6. Although there have been known crystalline silicates having  $\text{SiO}_2$  to  $\text{M}_2\text{O}$  ratios (wherein M is Na) of 1.9 to 4.0, crystalline silicates having silicone dioxide to alkali metal oxide ratios exceeding 2.6 are often unusable as the constituent of the high-density powdered detergent composition of the present invention.

Examples of the crystalline silicate to be favorably used in the present invention include those having the following compositions (II) and (III):



wherein M is a Group Ia element of the periodic table; Me is at least one element selected from among Group IIa, IIb, IIIa, IVa and VIII elements of the periodic table; y/x is a number of 0.5 to 2.6, preferably 1.5 to 2.2; z/x is a number of 0.01 to 1.0, preferably 0.02 to 0.9, still preferably 0.02 to 0.5; w is a number of 0 to 20; and n/m is a number of 0.5 to 2.0, and



wherein M is alkali metal; x' is a number of 1.5 to 2.6; and y' is 0 to 20.

Specific examples of the crystalline silicate represented by the above formula (II) are disclosed in JP-A 5-279013 and 7-89712 and US 5427711 corresponding to them. The crystalline silicates disclosed therein can be used in the present invention.

The crystalline silicate represented by the formula (II) exhibits a pH of 11 or above in the state of a 0.1% by weight aqueous dispersion. That is, it is excellent in alkalinizing power (power of making an aqueous system basic by being dispersed or dissolved in the system). Further, the crystalline silicate exhibits a particularly high buffer capacity in the alkaline (basic) region and its buffer capacity is higher than that of sodium carbonate or potassium carbonate.

The crystalline silicate represented by the formula (II) has an ion exchange capacity of at least 100 CaCO<sub>3</sub> mg/g, preferably 200 to 600 CaCO<sub>3</sub> mg/g, and therefore serves as one of the substances capable of capturing ions in the present invention.

As described above, the crystalline silicate represented by the formula (II) exhibits both a high alkalinizing power and a high buffer capacity in the alkaline (basic) range, and further has a high ion exchange capacity.

It is preferable that the crystalline silicate represented by the formula (II) have a mean particle diameter of 0.1 to 100 μm, still preferably 1 to 60 μm. When the mean particle diameter exceeds 100 μm, the development of the ion exchange power of the silicate will be so slow as to bring about a lowering in the detergency, while when it is less than 0.1 μm, the resulting silicate will exhibit high absorptivity for moisture and CO<sub>2</sub> owing to its enhanced specific surface area to result in remarkably deteriorated quality. The term "mean particle diameter" used in this description refers to a median diameter of particle size distribution.

The crystalline silicate having such a mean particle diameter can be produced by pulverizing crystalline silicate particles of somewhat large sizes by the use of a vibration mill, a hammer mill, a bowl mill, a roller mill or other pulverizer.

Next, the crystalline silicate represented by the formula (III) will be described.

Among the crystalline silicates represented by the formula (III), those wherein x' is 1.7 to 2.2 and y' is 0 are preferable. Further, those having a cation exchange capacity of 100 to 400 CaCO<sub>3</sub> mg/g are usable in the present invention. In the present invention, the crystalline silicate represented by the formula (III) serves as one of the substances capable of capturing ions.

As described above, the crystalline silicate represented by the formula (III) exhibits both a high alkalinizing power and a high buffer capacity in the alkaline (basic) range, and further has a high ion exchange capacity.

The crystalline silicate represented by the formula (III) can generally be prepared by firing amorphous glassy sodium silicate at 200 to 1000°C to crystallize it, though the production processes therefor are disclosed in JP-A 60-227895 and US 4664839 corresponding thereto. Details of the production thereof are described also in, for example, Phys. Chem. Glasses, Z, p.p.127-138 (1966). Z. Kristallogr., 129, p.p.396-404 (1969) and so on. Further, the crystalline silicate represented by the formula (III) is commercially available, e.g., under the trade name of "Na-SKS-6" (composition: δ-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>) from Hoechst Ltd. as powder or granule.

It is preferable that the crystalline silicate represented by the formula (III) as well as the one represented by the formula (II) have a mean particle diameter of 0.1 to 100 μm, still preferably 1 to 60 μm.

In the present invention, the crystalline silicates represented by the formula (II) and those represented by the formula (III) may be used each alone or as a mixture of two or more of them. Further, it is preferable that the silicate(s) account for 30 to 100% by weight, still preferably 70 to 100% by weight of the alkaline substances contained in the composition.

From the standpoints of the detergency of the composition and the physical properties thereof as powder, the crystalline silicate may be contained in the composition in an amount of 0 to 40% by weight, preferably 5 to 35% by weight.

(Other builders)

A builder has both the effect of separating solid-particle dirt from clothes and dispersing it in a washing solution and the effect of preventing the solid-particle dirt thus dispersed from redepositing on clothes (resoiling clothes). In order to attain such effects of a builder sufficiently, it is preferable that the high-density powdered detergent composition contain a polycarboxylate having an average molecular weight of hundreds to a hundred thousand, for example, a random copolymer comprising at least one monomer selected from the group consisting of maleic acid, maleic anhydride and salts of maleic acid with sodium, potassium and ammonium and at least one monomer copolymerizable therewith (such

as C<sub>1</sub>-C<sub>8</sub> olefin, acrylic acid, methacrylic acid, itaconic acid or methallylsulfonic acid), or a homopolymer represented by the following formula (V):



wherein P is a constituent unit of a homopolymer resulting from a homopolymerizable monomer; and 1 is a value giving a homopolymer having an average molecular weight of hundreds to a hundred thousand. In this homopolymer, at least part of the constituent units (P's) are converted into at least one salt selected from the group consisting of sodium salt, potassium salt and ammonium salt.

In the above formula (V), the constituent unit of the homopolymer is one resulting from acrylic acid, methacrylic acid, maleic acid or the like.

In the present invention, it is preferable that one or more members selected from among the above random copolymers and the homopolymers of the formula (V) be used in a total amount (or in an amount, when only one of them is used) of 1 to 8% by weight, still preferably 2 to 6% by weight based on the total amount of the detergent composition containing the same. Among these polycarboxylates, salts of acrylic acid/maleic acid copolymers or polyacrylic acid with Na, K and/or NH<sub>4</sub> are particularly excellent. The average molecular weight thereof is preferably 1000 to 100000, still preferably 1000 to 80000.

In addition to the above builders, the high-density powdered detergent composition of the present invention can contain also the following inorganic or organic builders.

#### (I) Inorganic builders

- 1) alkaline salts such as sodium carbonate, potassium carbonate, sodium bicarbonate, sodium sulfite and sodium sesquicarbonate,
- 2) salts of phosphoric acids such as orthophosphoric acid, pyrophosphoric acid and tripolyphosphoric acid with alkali metals such as sodium and potassium,
- 3) neutral salts such as sodium sulfate

#### (II) Organic builders

- 1) alkali metal salts of phosphonic acids such as ethane-1,1-diphosphonic acid and ethane-1,1,2-triphosphonic acid,
- 2) polyelectrolytes such as polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone, carboxymethylcellulose and polyaspartic acid,
- 3) alkali metal salts of organic acids such as diglycolic acid and oxydisuccinic acid.

#### (Other components)

The high-density powdered detergent composition of the present invention may further contain other conventional components for detergents at need, and such components include bleaching agents, bleaching activators, enzymes, enzyme stabilizers, bluing agents, anticaking agents, antioxidants, fluorescent dyes and perfumes.

Examples of the bleaching agents include sodium percarbonate, sodium perborate (with its monohydrate being preferable) and sodium sulfate-hydrogen peroxide adduct, among which sodium percarbonate is particularly preferable.

Examples of the bleaching activators include tetraacetythylenediamine, acetoxymethanesulfonic acid salts, organic peroxy acid precursors described in JP-A 59-22999 and US 4412934 corresponding thereto, JP-A 63-258447 and US 4751015 corresponding thereto, and JP-A 6-316700, and metal catalysts wherein transition metals are stabilized with sequestering agents.

The enzyme to be optionally used in the present invention (which essentially exhibits enzymatic activity in the washing step) is preferably protease, esterase, lipase, carbohydrase, nuclease or pectinase.

Specific examples of the protease include pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN, papain, bromelain, carboxypeptidases A and B, aminopeptidase and aspergillopeptidases A and B, which are commercially available under the trade names of "Sabinase" and "Alkarase" (from Novo Industri), "API21" (from Showa Denko, K.K.) and Maxacal (from Gist-Brocades); and proteases K-14 and K-16 described in JP-A 5-25492 and US 5312561 corresponding thereto.

Specific examples of the esterase include gastric lipase, pancreatic lipase, plant lipase, phospholipase, choline esterase and phosphatase.

The lipase may be a commercially available one such as "Lipolase" (a product of Novo Industri).

Specific examples of the carbohydrase include cellulase, maltase, saccharase, amylase, lysozyme,  $\alpha$ -glycosidase

and  $\beta$ -glycosidase.

The cellulase may be "Celluzyme" (a product of Novo Industri) or a cellulase described in claim 4 of JP-A 63-264699 and US 4822516 and 4978470 corresponding thereto, while the amylase may be "Termamyl" (a product of Novo Industri) or the like.

The enzyme stabilizers include reducing agents (such as sodium sulfite and sodium hydrogensulfite), calcium salts, magnesium salts, polyols, boron compounds and so on.

Various bluing agents may also be added to the detergent composition at need. In particular, bluing agents whose chemical structures are described in JP-B 49-8005, 49-26286 and 53-45808 are preferably used.

Examples of the anticaking agents include p-toluenesulfonic acid salts, xylenesulfonic acid salts, acetic acid salts, sulfosuccinic acid salts, talc, finely powdered silica, clay and magnesium oxide. Among finely divided silica and so on, porous ones are usable also as carriers for nonionic surfactants. Further, clay (specifically, smectite clay) is effective also as softener.

Examples of the antioxidants include t-butylhydroxytoluene, 4,4'-butylidenebis(6-t-butyl-3-methylphenol), 2,2'-butylidenebis(6-t-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1'-bis(4-hydroxyphenyl)cyclohexane.

Further, the detergent composition may contain a fluorescent dye in an amount exceeding 0% by weight but up to 1% by weight, the fluorescent dye being at least one member selected from the group consisting of 4,4'-bis(2-sulfostyryl)biphenyl salts, 4,4'-bis(4-chloro-3-sulfostyryl)biphenyl salts, 2-(styrylphenyl)naphthothiazole derivatives, 4,4'-bis(triazol-2-yl)stilbene derivatives and bis(triazinylamino) stilbenedisulfonic acid derivatives.

Examples of the perfumes include conventional ones for detergents as described in JP-A 63-101496.

The high-density powdered detergent composition of the present invention takes a powdery or granular form. The process for producing the composition is not particularly limited, but may be any known one. The bulk density of the composition can be enhanced by a process of spraying a nonionic surfactant on spray-dried particles, a process of making a powdery component containing an oil-absorbing carrier occlude a nonionic surfactant, or by referring to the processes described in JP-A 61-69897, 61-69899 and 61-69900, JP-A 2-222498 and US 5052122 corresponding to it, JP-A 2-222499, JP-A 3-33199 and EP-A 339996 corresponding to it, JP-A 5-86400 and US 5282996 corresponding to it, and JP-A 5-209200 and US 5468516 corresponding to it.

When a crystalline aluminosilicate is used as the component (d), a small portion of the crystalline aluminosilicate may be added during the granulation or just before the completion of the granulation as the surface modifier for the granules. When a crystalline silicate is used, it is preferable that the silicate be added in the step of enhancing the bulk density or dry-blended with the granules. When an alkali metal carbonate is used, it may be added to the slurry or at any step during the granulation, or dry-blended with the granules.

It is desirable from the standpoint of the physical properties of the composition as powder that the high-density powdered detergent composition of the present invention has a mean particle diameter of 200 to 1000  $\mu\text{m}$ , particularly 200 to 600  $\mu\text{m}$ . Further, the detergent composition of the present invention has a bulk density of 0.6 to 1.2 g/ml, preferably 0.6 to 1.0 g/ml.

The detergent composition of the present invention may be used in a suitable concentration, which depends on which of several washing methods (such as machine washing and immersion) is employed, quantity of clothes or water, extent of stains, operating conditions of the machine, or the like. In machine washing, for example, the composition may be used in a concentration of 0.03 to 0.3% by weight.

As described above, the present invention can provide a high-density powdered detergent composition which contains both an organic builder excellent in biodegradability and an inorganic builder and is enhanced in detergency.

Example:

The present invention will now be described in detail by referring to the following Example, though the present invention is not limited by it.

#### Example 1

(Preparation of high-density powdered detergent compositions)

Composition 1 specified in Table 1 was prepared according to the following procedure.

An aqueous slurry having a solid content of 60% by weight was prepared by using 0.5 kg of MGDA, 1.0 kg of crystalline aluminosilicate, 0.8 kg of FA, 0.3 kg of polysodium acrylate and 1.0 kg of soda ash (sodium carbonate). The obtained slurry was subjected to spray drying. The particles thus obtained were put in a Lödige mixer (mfd. by Matsuzaka Giken K.K.), followed by the addition thereto of 1.0 kg of porous silica, 0.5 kg of crystalline aluminosilicate, 2.0 kg of silicate (II), 0.1 kg of an enzyme, the balance of Glauber's salt and 0.05 kg of a fluorescent dye [i.e., 4,4'-bis(2-sul-



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fosteryl)biphenyl salt]. The resulting mixture was agitated, while 2.0 kg of AE-1 and 0.1 kg of PEG which had been pre-heated to 70°C were gradually dropped into the mixture. Thus, the mixture was granulated. Then, 0.5 kg of crystalline aluminosilicate was added to the granulated mixture, and the obtained mixture was further subjected to granulation. Thus, a high-density powdered detergent composition having a mean particle diameter of 430 µm and a bulk density of 0.810 g/ml was obtained.

The other high-density powdered detergent compositions were also prepared according to the same procedure as that described above except that components listed in Tables 1 to 3 were used in proportions specified in Tables 1 to 3. The obtained powdered detergent compositions had bulk densities of  $0.800 \pm 0.050$  g/ml.

The high-density powdered detergent compositions were subjected to the following detergency test. The results are given in Tables 1 to 3.

(Detergency test)

(Preparation of artificially stained cloth)

One kilogram of a mixture prepared by adding 5 parts by weight of carbon black to 100 parts by weight of a fatty acid/paraffin mixture having the following composition was dispersed and dissolved in 80 l of tetrachloroethylene. Then, shirting cloth #2023 was immersed in the obtained solution to thereby stain the cloth. The resulting stained cloth was dried and freed from the tetrachloroethylene.

Composition of the fatty acid/paraffin mixture:

oleic acid	20% by wt.
palmitic acid	20% by wt.
liquid and solid paraffins	60% by wt.

The artificially stained cloth prepared above was cut into pieces (10 cm × 10 cm) and the pieces were used in the following experiment.

(Washing procedure)

The pieces of the artificially stained cloth prepared above were washed by the use of a Terg-O-Tometer (rotational speed: 100 rpm) and the detergent compositions of the present invention or comparative ones listed in Tables 1 to 3 under the following conditions.

Washing conditions

bath ratio: 1/60,  
temp. of water: 25°C  
washing time: 15 min,  
rinsing: with tap water for 5 min,  
hardness of water: 4°DH (calcium hard water), and  
detergent concn.: 0.0667 wt.%

(Calculation of rate of cleansing)

The rate of cleansing of the stained cloth was calculated as follows: The reflectivities at 550 nm of the unstained cloth and the stained cloth before and after the washing by the use of a self-colorimeter (mfd. by Shimadzu Corporation), and the rate (D%) of cleansing was calculated according to the following formula.

$$D = [(L_2 - L_1) / (L_0 - L_1)] \times 100$$

wherein  $L_0$  is the reflectivity of unstained cloth;  $L_1$  is that of stained cloth before washing; and  $L_2$  is that thereof after washing.

Table 1

			Compn. No.									
			1	2	3	4	5	6	7	8	9	10
Formu- lation (wt. %)	Compo- nent a	MGDA	5	10	15	20	10	10	10	10	10	10
	Compo- nent b	AE-1	20	20	20	20	20	25	30	33	20	20
	AE-3	AE-2	0	0	0	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0	0	0
	Compo- nent c	LAS	0	0	0	0	0	0	0	0	0	0
		AS	0	0	0	0	0	0	0	0	0	0
		FA	8	8	8	8	8	8	8	8	8	8
	compo- nent d	cryst. alumino- silicate (zeolite)	20	15	10	5	15	10	5	2	15	15
		silicate (II)	20	20	20	20	20	20	20	20	10	0
	silicate (III)	0	0	0	0	0	0	0	0	0	10	20
	JIS No. 2 sodium silicate	0	0	0	0	10	0	0	0	0	10.0	0
	other compo- nents	polysodium acrylate	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
		PEG	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		porous silica	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
sodium carbonate		10.0	10.0	10.0	10.0	0	10.0	10.0	10.0	0	10.0	
common component		bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	
sum total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
Result	rate of cleansing (%)		72.5	73.5	75.0	74.0	73.2	72.0	71.3	70.1	73.3	73.1

		Compn. No.									
		11	12	13	14	15	16	17	18	19	
Formulation (wt. %)	component a	MGDA	10	10	10	10	10	10	10	10	
	component b	AE-1	15	20	20	20	20	20	20	20	
		AE-2	0	0	0	0	0	0	0	0	
	AE-3		0	0	0	0	0	0	0	0	
	component c	LAS	0	0	0	8	0	0	0	0	
		AS	0	0	0	0	8	0	0	0	
		FA	8	4	2	0	0	8	8	8	
	component d	cryst. aluminosilicate (zeolite)	20	19	21	15	15	15	15	15	
	silicate (II)		20	20	20	20	20	20	30	20	
	silicate (III)		0	0	0	0	0	0	0	0	
	JIS No. 2 sodium silicate		0	0	0	0	0	3	10	0	
	other components	polysodium acrylate	3.0	3.0	3.0	3.0	3.0	0	3.0	3.0	3.0
		PEG	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		porous silica	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
		sodium carbonate	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
common component		bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	
sum total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
Result	rate of cleansing (%)	70.4	72.2	70.1	73.0	72.7	71.0	70.8	74.1	70.5	

Table 3

	component	Compn. No.										
		20	21	22	23	24	25	26	27	28		
Formulation (wt. %)	a	MGDA	10	5	0	0	10	10	10	10		
	component	AE-1	20	20	20	20	20	20	20	20	0	0
	b	AE-2	0	0	0	0	0	0	0	0	0	0
	AE-3		0	0	0	0	0	0	0	0	0	0
	component	LAS	0	0	0	0	0	0	0	0	0	0
	c	AS	0	0	0	0	0	0	0	0	0	0
		FA	8	8	8	8	0	20	20	20	8	8
	component	cryst. aluminosilicate (zeolite)	15	20	25	0	15	15	5	23	15	15
	d											
	silicate (II)		0	0	20	20	18	8.0	20	0	20	20
	silicate (III)		0	0	0	0	0	0	0	0	0	0
	JIS No. 2 sodium silicate		20	20	0	25	0	0	0	0	0	0
other components	polysodium acrylate	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	PEG	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	porous silica	10.0	10.0	10.0	10.0	12.0	10.0	10.0	10.0	10.0	10.0	10.0
	sodium carbonate	10.0	10.0	10.0	10.0	10.0	10.0	8.0	10.0	10.0	10.0	10.0
	common component	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance	bal-ance
	sum total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Result	rate of cleansing (%)	67.0	65.1	64.5	58.5	66.4	63.1	65.5	58.2	54.6		

notes)

- MGDA: trisodium salt of methylglycine-N,N'-diacetic acid
- AE-1: polyoxyethylene dodecyl ether (HLB value: 13.1)
- AE-2: polyoxyethylene dodecyl ether (HLB value: 11.2)
- AE-3: polyoxyethylene dodecyl ether (HLB value: 15.1)

The HLB values of AE-1 to AE-3 were calculated by  
Griffin's method.

- LAS: sodium salt of linear alkyl ( $C_{12}$ ) benzenesulfonic acid
- AS: sodium salt of dodecyl alcohol sulfate
- FA: sodium salt of tallow fatty acid
- cryst. aluminosilicate:

(composition:  $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ , mean particle diam.:

2  $\mu m$ , ion exchange capacity: 290  $CaCO_3$  mg/g)

- silicate (II): crystalline silicate represented by the  
formula (II) (see "Detailed Description of the  
Invention")

[Composition:  $M_2O \cdot 1.8SiO_2 \cdot 0.02M'O$  (wherein M is Na and K,  
K/Na being 0.03; and M' is Ca and Mg, Mg/Ca being 0.01),  
mean particle diam: 30  $\mu m$ , ion exchange capacity: 305  
 $CaCO_3$  mg/g]

- silicate (III): crystalline silicate represented by the  
formula (III) (see "Detailed Description of the  
Invention")

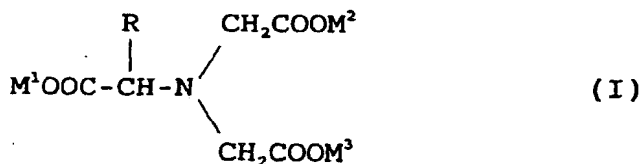
(Composition:  $Na_2O \cdot 2SiO_2$ , mean particle diam: 30  $\mu m$ , ion

exchange capacity: 224 CaCO<sub>3</sub> mg/g)

- polysodium acrylate: sodium salt of polyacrylic acid  
having an average molecular weight of 8000
- PEG: polyethylene glycol having an average molecular weight  
of 7000
- porous silica: Tixolox 25 (a product of Kofran Chemical)
- common component: comprising 1 wt. % of an enzyme mixture  
[comprising API-21H (a product of Showa Denko K.K.),  
Lipolase 100 T (a product of Novo Nordisk), Celluzyme  
0.1T (a product of Novo Nordisk), and Termamyl 60T (a  
product of Novo Nordisk) at a weight ratio of 2 : 1 :  
1 : 1], 0.5 wt. % of a fluorescent dye and the balance  
(such an amount as to make a total of 100 wt. %) of  
Glauber's salt, each content being based on the total  
weight of the detergent composition.

#### Claims

1. A high-density powdered detergent composition which has a bulk density of 0.6 to 1.2 g/ml and which comprises 0.5 to 30% by weight of (a) a glycine-N,N-diacetic acid derivative represented by the following formula (I), 5 to 45% by weight of (b) a nonionic surfactant having an HLB (Hydrophile Lypophile Balance) value of 10.5 to 15.0, 0.5 to 18% by weight of (c) an anionic surfactant and 1 to 30% by weight of (d) an aluminosilicate, each percentage being based on the total weight of the composition, and the weight ratio of the component (b) to the component (c) lying between 90 : 1 and 60 : 40:



wherein R is C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>18</sub> alkenyl; and M<sup>1</sup>, M<sup>2</sup> and M<sup>3</sup> are each H, Na, K or NH<sub>4</sub>.

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2. The high-density powdered detergent composition according to claim 1, wherein the component (c) is a salt of a higher fatty acid having 10 to 18 carbon atoms.
3. The high-density powdered detergent composition according to claim 1, wherein the weight ratio of the component (b) to the component (c) lies between 95 : 5 and 79 : 21.
4. The high-density powdered detergent composition according to claim 1, wherein the content of the component (a) is 2 to 15% by weight.
5. The high-density powdered detergent composition according to claim 1, wherein the component (b) has an HLB value of 11 to 14.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/00110

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl <sup>6</sup> C11D1/83, C11D3/33, C11D3/08, C11D3/37, C11D17/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl <sup>6</sup> C11D1/02-1/38, 1/66-1/831, 3/26-3/33, 17/06, C07C229/16		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
CAS ONLINE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, 94/29421, A1 (BASF AG.), December 22, 1994 (22. 12. 94), Claim & JP, 8-511255, A & DE, 4319935, A1 & EP, 703971, A1	1 - 5
Y	JP, 58-51994, B (Kureha Chemical Industry Co., Ltd.), November 19, 1983 (19. 11. 83), Claim; column 3, line 12 to column 5, line 23 & EP, 30461, A & CA, 1120817, A & US, 4349447, A & DE, 3062987, A	1, 5
Y	JP, 6-9999, A (Kao Corp.), January 18, 1994 (18. 01. 94), Claim (Family: none)	1 - 5
A	JP, 2-229894, A (Kao Corp.), September 12, 1990 (12. 09. 90), Claim (Family: none)	1 - 5
A	JP, 2-163200, A (BASF AG.),	1 - 5
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search April 10, 1997 (10. 04. 97)		Date of mailing of the international search report April 22, 1997 (22. 04. 97)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer  Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	June 22, 1990 (22. 06. 90), Claim; refer to table 1 & EP, 356974, A & DE, 3829847, A & AU, 8940956, A & US, 4997587, A	

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